

# Generating the Right Data: Determination of Aroclors Versus PCB Congeners

Prepared for the U.S. Department of Energy  
Assistant Secretary for Environmental Management

Project Hanford Management Contractor for the  
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**Generating the Right PCB Data:  
Determination of Aroclors Versus PCB Congeners – 8075**

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**ABSTRACT**

Polychlorinated biphenyls (PCBs) are a major environmental concern due to their ubiquity and tendency to bio-accumulate, as well as their persistence and toxicity. As the cleanup of waste and contaminated soil progresses at U.S. Department of Energy (DOE) sites, the costs for accurate PCB data are increasing. PCBs are actually a broad name for a group of 209 individual compounds known as congeners. PCBs were originally produced in the United States as specific mixtures of congeners known as Aroclors<sup>1</sup>. PCBs can be analyzed and quantified either as Aroclor mixtures or as individual congeners. Aroclor analysis, which is the more common analytical method applied to PCBs, has been in use for decades, and in general, most cleanup regulations are based on total PCB concentrations using Aroclor analyses. Congener analysis is relatively new to environmental cleanup and restoration due to both technical issues and associated cost. The benefits of congener analysis are that it allows a more direct analysis of the risk of the PCBs. The World Health Organization (WHO) has identified twelve specific congeners as *dioxin-like* with toxicity ranging from 0.00003 to 0.1 times the standard 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) toxicity. This paper defines Aroclors and congeners and compares the current application and usefulness of the two analytical methods for environmental restoration and cleanup. A strategy for the best use of the two methods to optimize overall characterization cost is presented. As part of the strategy, a method using the data from Aroclor analyses to calculate 2,3,7,8-TCDD toxicity equivalent concentrations is also presented.

**INTRODUCTION**

Polychlorinated biphenyls (PCBs) represent a class of synthetic organic molecules that are characterized by two benzene rings linked together (biphenyl) with from 1 to 10 of the hydrogen atoms replaced by chlorine atoms. There are 209 distinct PCB congeners. PCBs are problematic due to their relative persistence in the environment and the evidence that at least some of the PCB compounds exhibit certain toxicity and potential carcinogenic or mutagenic activity. In 1976, the U.S. Environmental Protection Agency (EPA), through the *Toxic Substances Control Act* (TSCA), prohibited manufacturing and commercial use of PCBs and regulated PCB disposal [1].

PCBs have found their way into the environment in several ways: one pathway has been inadvertently spilling or releasing commercial PCB mixtures known as Aroclors<sup>1</sup>. In the United States, all PCBs were produced by a single manufacturer under the trade name Aroclor. There are several specific Aroclor mixtures, each with a known distribution of various PCB congeners.

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<sup>1</sup> Aroclor is a trade name of Monsanto.

Formal congener nomenclature can get unwieldy so a numbering scheme (BZ #) [2] has been defined that assigns a unique number from 1-209 to each individual PCB congener.

### Use at Hanford

The history of the Hanford Site goes back to the early 1940s when the site was established as part of the Manhattan Project. From that time through the 1970s, Aroclors were used commercially in electrical substations, transformers, capacitors, hydraulic fluid, roofing material, paints, coatings, and caulking [3]. Residual concentrations of Aroclors have been detected in the sludge in Hanford's waste tanks, as well as the Hanford Site's soil and various disposal-facility samples. As more waste-handling facilities are closed, PCBs will surely be considered in various risk-based decisions affecting cleanup.

### Chemical Analysis Methods

Two methods are typically used to analyze for PCBs in environmental samples. The total PCB or Aroclor method (e.g., SW-846 Method 8082) [4] extracts PCBs from a sample, analyzes the extract by gas chromatography (GC), and then uses a certain subset of peaks to determine the concentration of the PCB mixture. A pattern-recognition technique is used to qualitatively determine whether or not an Aroclor mixture is present; then a set of standards using that particular Aroclor is used for quantification. This method can measure the total amount of PCBs present in a sample, but has only limited ability to identify and quantify each of the 60-80 individual PCB congeners within any Aroclor mixture. Rather, the analyst uses the presence and ratio of a select subset of individual PCB congeners to identify which Aroclor is represented. The total amount of material can be related to a total amount of Aroclor. Individual PCB congener concentrations are not reported.

If total PCBs are requested, or if the detected PCBs do not conform to a known Aroclor mixture, then another set of up to 19 PCB congeners may be used for total PCB quantification and the result is reported as *individual congeners or total PCBs*. It is critical for the requestor to discuss the application of the results with the laboratory analyzing the sample so that the format of the results correlates with the environmental requirement (i.e., total PCB, Aroclor, or individual congener).

The second approach is the congener-specific method (e.g., USEPA Method 1668a) [5]. This process uses a high-resolution gas chromatograph/mass spectrometer (GC/MS) to determine the concentration of each individual PCB congener in the sample. There are no presumptions regarding the PCB source material, whether it is an Aroclor or PCBs from combustion or some other source. The results are concentrations of each individual congener, subject to some technical limitations on the ability to resolve a handful of co-eluting congeners.

The two methods differ considerably in reported parameters, detection limits, availability and cost. The total PCB/Aroclor method is readily available and relatively inexpensive, but may not provide detection limits required for making decisions about closure-related activities. On the other hand, the congener-specific method can provide low detection limits for individual constituents. However, it is nearly an order of magnitude more expensive than the other method.

The congener-specific method is also more difficult to perform, and requires much more expensive equipment, individual radio-labeled compound standards, and expertise that is only available at a handful of environmental laboratories.

### Regulatory Considerations

Until recently, chemical analysis for total PCBs or Aroclors has been compatible with environmental regulations in that the regulatory criteria have traditionally been referenced to total PCB concentration or specific Aroclor concentration. Thus, results from Method 8082 could be used directly to determine compliance. However, as regulatory strategies evolve and regulatory criteria change, the Method 8082 performance may not be able to determine Aroclors at low enough concentrations to conclusively demonstrate that certain risk-based soil-cleanup levels are met.

Recent changes in regulatory approach have altered the way some PCB contamination might be regulated. One significant evolution is based on identifying a subset of PCB molecules as having toxicological properties comparable to chlorinated dibenzo-p-dioxins. According to information provided by the World Health Organization (WHO)[6], the health risk of these 12 dioxin-like PCB congeners can be related to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) through a Toxicity Equivalency Factor (TEF). By multiplying the concentration of each of the 12 PCB congeners by its own TEF, one can derive the Toxicity Equivalent concentration (TEQ) of 2,3,7,8-TCDD that would represent an identical health risk. If each of the 12 PCB congener's TEQs are added together, one can calculate the concentration equivalent of 2,3,7,8-TCDD for the entire PCB mixture. These calculations are shown as equations (Eq. 1) and (Eq. 2).

$$(\text{Individual PCB congener concentration}) \times \text{TEF} = (\text{congener 2,3,7,8-TCDD TEQ}). \quad (\text{Eq. 1})$$

$$\text{Sum of all 12 (congener TEQ)} = (\text{sample 2,3,7,8-TCDD TEQ}). \quad (\text{Eq. 2})$$

Table I shows an example calculation of congener TEQ and sample TEQ using concentration results for the 12 dioxin-like PCB congeners in a hypothetical sample where each congener is present at the nominal reporting limits for Method 1668a.

Table I. Example Calculation Using Concentration Results for the 12 Dioxin-Like PCB Congeners in a Hypothetical Sample Where Each Congener Is Present at the Nominal Method 1668a Reporting Limits

Dioxin-like PCB Congener	TEF	Nominal Method 1668a reporting limits (pg/g)	Calculated Method TEQ (pg/g)
77	0.0001	50	0.005
81	0.0003	50	0.015
105	0.00003	20	0.0006
114	0.00003	50	0.0015
118	0.00003	50	0.0015
123	0.00003	50	0.0015
126	0.1	50	5
156	0.00003	50	0.0015
157	0.00003	50	0.0015
167	0.00003	50	0.0015
169	0.03	50	1.5
189	0.00003	50	0.0015
Total			6.531

pg/g – picograms per gram

Note: Calculated 2,3,7,8-TCDD toxic equivalent in this hypothetical sample is 6.5 pg/g. Note also the dominance of PCB 126 and 169 to the total calculated equivalent toxicity due to high Toxicity Equivalent Factors.

The challenge in chemically analyzing environmental samples is to determine the concentrations of each of the 12 dioxin-like congeners from within a complex mixture of PCBs at the very low levels driven by the 2,3,7,8-TCDD regulatory limits for maximum concentration. Method 8082 cannot determine all of these individual congeners within a sample containing Aroclor mixtures.

## PCB ANALYSIS APPLICATION TO CURRENT AND FUTURE HANFORD SITE REMEDIATION CRITERIA

Hanford is engaging in various facility and individual cleanup actions under the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) regulatory umbrella. Until the present, residual PCB cleanup levels have been developed for specific Aroclors, or total PCBs, without consideration of individual congeners.

As previously mentioned, state and federal regulators are now looking at individual PCB congeners within their closure and cleanup regulatory framework. Within the state of Washington, the Washington State Department of Ecology (Ecology) has amended its *Model Toxic Substances Control Act* (MTCA) regulations to include consideration of the 12 WHO dioxin-like congeners in cleanup actions under MTCA authority [7].

MTCA regulations offer several ways for the regulated community to determine appropriate cleanup levels on a graded approach – from simple lookup screening values, through a system of risk-based fate, transport and exposure calculations that consider generic or site-specific parameters.

Hanford scientists have developed a table of values (called the CLARC Table) for various cleanup limits based on Washington State's MTCA calculations for fate, transport, and exposure calculations. Included in Hanford's CLARC table are limits for total PCBs, specific Aroclors, and 2,3,7,8-TCDD in various media, including two direct-exposure-to-soil scenarios (MTCA Method B and C), and soil levels protective of underlying groundwater.

Table II shows cleanup levels calculated from the Hanford CLARC Table.

Table II. MTCA Cleanup Levels for Aroclors and Total PCBs (from Hanford's CLARC table, 2005)

PCB	Method B Soil (mg/kg)	Method C Soil (mg/kg)	Soil Protective of Groundwater (mg/kg)
Aroclor 1221			9.20E-03
Aroclor 1232			9.20E-03
Aroclor 1242			3.94E-02
Aroclor 1248			3.86E-02
Aroclor 1254			6.64E-02
Aroclor 1260			7.21E-01
PCB total	5.00E-01	6.56E+01	3.09E+00
PCB total (central estimate slope factor)	1.00E+00	1.31E+02	3.09E+00
2,3,7,8-TCDD			6.7E-06

The cleanup levels that are shaded in Table II may be below, or very close to, typical Method 8082 detection levels of 50-70µg/kg.

It may be possible to take advantage of the relatively organic-free and sandy-textured soils within the Hanford area to challenge the laboratories to achieve lower detection limits using Method 8082. This could be done by using larger initial sample sizes and modifying GC parameters and equipment to inject larger volumes. It is thought that improvements by one-to-two orders of magnitude may be achievable. Even an improvement of a factor of 10 (to 5-7 µg/kg) would enable Method 8082 to meet all default MTCA PCB-related soil cleanup criteria.

Method 1668a can determine each of 209 individual PCB congeners at much lower detection limits than Method 8082. Reported detection limits for each of the 12 dioxin-like congeners should theoretically enable the calculation of 2,3,7,8-TCDD toxicity equivalent concentrations that are low enough to demonstrate compliance with the MTCA-derived cleanup limits. However, further investigation reveals some concerns.

Table I shows the calculation that would arise from each of the 12 congeners present at the detection limit of the 1668 method. Note that the resulting equivalent concentration of 6.5 pg/g is indeed below, but very close to, the MTCA Method B 2,3,7,8-TCDD cleanup level of 6.7 pg/g. Sample interferences or matrix considerations may prevent a laboratory from meeting the theoretical method detection limits. In this case, the 1668 method would also not be able to clearly demonstrate compliance with the MTCA requirement.



## INDIRECT CALCULATED CONGENER CONCENTRATION

The EPA has recognized the Aroclor/congener method dilemma and has issued internal guidance to continue to characterize sites using Method 8082, but to supplement the sampling, in certain cases, with some percentage of individual congener analysis [8]. This approach would represent a compromise of the use of a proven method (8082) with higher detection limits with a much more expensive individual congener method with the ability to detect individual PCB congeners of interest at low detection limits. The approach presented in this paper is consistent with this EPA guidance, but adds an additional calculation, arguably justified by unique Hanford conditions, which potentially can increase the information value of the data.

Rushneck, *et al* [9], have determined the concentrations of the 12 dioxin-like congeners in Aroclors to the sub-ppm level (Table III).

Table III. Dioxin-like PCB Congener Concentrations in Commercial Aroclors\*  
(all concentrations in  $\mu\text{g/g}$  or ppm)

PCB Congener	WHO TEF	Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268
77	0.0001	12.6	2150	40.9	2590	4440	174	33.8	84.6	36.1
81	0.0003	0.51	111	1.96	156	221	16.4	3.33	4.63	1.35
105	0.00003	55.9	3030	69.5	4840	17300	33800	434	764	107
114	0.00003	4.04	248	6.03	443	1320	1930	17	46	5.86
118	0.00003	88.1	4460	110	6980	24200	78900	5610	1980	101
123	0.00003	3.33	164	4.72	277	806	1150	5.02	27.8	3.24
126	0.1	0.28	21	0.56	33.6	98	37.3	2.13	2.28	1.76
156	0.00003	7.49	90.7	3.72	255	654	8440	4860	946	17.6
157	0.00003	1.46	22	1.03	70.9	171	1870	252	63.8	7.92
167	0.00003	2.52	32.4	1.1	80.7	207	3100	1990	278	4.96
169	0.03	0.08	0.17	0.13	0.11	0.21	0.81	0.82	0.4	0.32
189	0.0003	1.17	4.36	0.12	4.53	11	246	1290	451	4.4

\*The table is adapted from Rushneck [9] with the modification that recently updated WHO TEFs have been added from [6].

Hanford Site chemical analysis databases contain more than 4,600 PCB determinations of environmental and waste samples, with approximately 102 results exceeding detection limits (positive hits). All of these positive hits were clearly definable as a single, specific Aroclor. The vast majority were Aroclor 1254, with the presence of Aroclor 1260 and 1248 found in isolated samples. No samples appeared to contain mixtures of more than one Aroclor. All results were generated using Method 8082.

Knowledge of the dioxin-like congener concentrations in Aroclors would, in theory, allow Aroclor concentrations to be directly related to a regulatory 2,3,7,8-TCDD risk-based threshold. To accomplish this, an Aroclor TEQ would have to be calculated based on the relative contribution of each dioxin-like congener within the Aroclor. In making the calculation, each of these calculated congener concentrations were multiplied by its respective TEF to determine the TEQ of each congener. Then the 12 TEQs were summed to find the sample TEQ to be

compared to the MTCA 2,3,7,8-TCDD cleanup level. This approach has been published by others [9]. Table IV shows the results of this calculation for three Aroclors, using the most recent WHO TEFs.

Table IV. Calculated Aroclor TEQ Using Dioxin-Like Congener Concentrations and 2005 WHO TEFs. (All Concentration Units, Including TEQ Are in µg/g or ppm.)

PCB Congener	WHO TEF	Aroclor 1248		Aroclor 1254		Aroclor 1260	
		Conc	TEQ	Conc	TEQ	Conc	TEQ
77	0.0001	4440	0.444	174	0.0174	33.8	0.00338
81	0.0003	221	0.0663	16.4	0.00492	3.33	0.000999
105	0.00003	17300	0.519	33800	1.014	434	0.01302
114	0.00003	1320	0.0396	1930	0.0579	17	0.00051
118	0.00003	24200	0.726	78900	2.367	5610	0.1683
123	0.00003	806	0.02418	1150	0.0345	5.02	0.000151
126	0.1	98	9.8	37.3	3.73	2.13	0.213
156	0.00003	654	0.01962	8440	0.2532	4860	0.1458
157	0.00003	171	0.00513	1870	0.0561	252	0.00756
167	0.00003	207	0.00621	3100	0.093	1990	0.0597
169	0.03	0.21	0.0063	0.81	0.0243	0.82	0.0246
189	0.0003	11	0.0033	246	0.0738	1290	0.387
Aroclor TEQ			11.7		7.7		1.0

For this approach to be applied to an actual cleanup site, the following would be required:

- The source of PCB contamination must be well characterized, including the specific contributions of the individual congeners of interest. If the contamination is clearly from a relatively unweathered Aroclor, then values in the literature may be used.
- The sample must not be a mixture of Aroclors, especially if the ratio of Aroclors varies across the site.
- There cannot be significant sample matrix interferences that would complicate analysis.

The issues of volatilization, dissolution, and degradation of Aroclors in the environment can be anticipated to be negligible in many Hanford locations. The Aroclors of interest (1248, 1254, and 1269) contain low concentrations of the lighter, less-chlorinated, PCB congeners that may be more volatile and water soluble than the more highly chlorinated congeners. In addition, the Hanford eco-region is desert shrub steppe, with very little rainfall (less than nine inches a year) and the soil is typically sandy, with little organic content. These conditions minimize percolating water dissolution, although some volatilization can be predicted.

Biodegradation of PCB compounds has also been identified as potentially possible. Although soil conditions at Hanford are not optimal for natural biodegradation of organic compounds, there may be some level of *in-situ* biodegradation of PCBs. The mechanism of biodegradation is through reductive de-chlorination of the para- and meta- chlorine positions preferentially. All of the 12 dioxin-like congeners have chlorines in both para positions. The removal of even one of

these chlorines through biological processes would result in a congener that is not on the list of 12 and would reduce overall mixture toxicity [10]. If biodegradation were to remove one or more meta-substituted chlorines, the resulting PCB compound would, in every case but one, be less toxic (using the TEF as the measure of toxicity). The single case that results in greater TEF is the removal of two meta-substituted chlorines from PCB 169 that would result in PCB 126. For the three Aroclors of interest at Hanford, the concentrations of PCB 169 are extremely low, even compared to the other 12 WHO congeners. Therefore, even if there were some degradation of this type, it would not be expected to alter the final results significantly.

At least some Hanford samples should be able to meet all the criteria for successful application of the alternative PCB calculation method using Method 8082 data, and the concomitant assumption that the original fractional congener content remains relatively unchanged from the original product.

The three Aroclors detected on the Hanford Site (1248, 1254, and 1260) can be analyzed via the described method. Table IV shows the calculated TEQ for each Aroclor at the Method 8082 reporting limit of 50 µg/kg. As shown in Table V, use of known congener concentrations and the less expensive Method 8082 can result in low TEQs for the 12 dioxin-like congeners. The calculated TEQs at the method detection limit are 0.58, 0.39, and 0.05 for Aroclor 1248, 1254, and 1260, respectively. These calculated TEQs are well under the MTCA cleanup criteria for soil and show that this method can clearly demonstrate that soil either meets or exceeds the challenging MTCA standard, without resorting to the expensive congener-specific analytical methods.

Table V. Hypothetical 2,3,7,8-TCDD Toxic Equivalent Concentration (TEQ) for Aroclors 1248, 1254, and 1260 Calculated at the Nominal Method 8082 Reporting Limit of 0.05 µg/g.

Aroclor	1248	1254	1260
Aroclor Conc (µg/g)	0.05	0.05	0.05
Aroclor TEQ (µg/g)	11.7	7.7	1
Equivalent 2,3,7,8-TCDD Conc (pg/g)	0.585	0.385	0.05
MTCA Criterion (pg/g)	6.7	6.7	6.7

## CONCLUSION

When Aroclor and total PCB cleanup criteria are applicable, then analyzing soil samples via reasonable-cost Method 8082 would provide sufficient data. In the event that typical Method 8082 detection levels are insufficient to demonstrate compliance, it is recommended to work with the laboratory to demonstrate lower reliable detection limits, using larger extraction volumes and increased gas chromatography injection volumes, along with any other enhancements that may be available. If PCBs are not detectable in samples using this method, then one may assume that, regardless of specific Aroclor, no current default MTCA soil cleanup limits would be exceeded.

However, where individual congener or 2,3,7,8-TCDD toxicity equivalent criteria are prescribed, an indirect calculation using Method 8082 data may be applicable. On the Hanford Site,

historical information may be compelling enough, in some locations, to justify assumptions that PCBs contamination is present as relatively unweathered Aroclors. Implementing Method 8082 analysis and performing the mathematical calculation of the 12 dioxin-like congeners using the EPA Aroclor composition data may be justifiable. In order to validate the hypotheses associated with Aroclor degradation or weathering, it may be prudent to perform validation split sampling and analysis of the 12 congeners using Method 1668 on a small subset of samples, selecting samples that are expected to contain measurable PCBs. Comparison of split samples using both methods will validate the use of the product Aroclor composition data for the specific use.

It must be noted that the discussions in this paper are applicable to soil samples; extrapolations of the concepts to biological tissue samples are not addressed. The potential for differential metabolism, bioaccumulation and biomagnifications of congeners may result in more profound changes in relative congener concentrations that are beyond the scope of this paper.

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